



SODIUM - METAL CHLORIDE BATTERIES



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THE 1991 NASA AEROSPACE BATTERY WORKSHOP**

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BATTERY SYSTEMS GROUP

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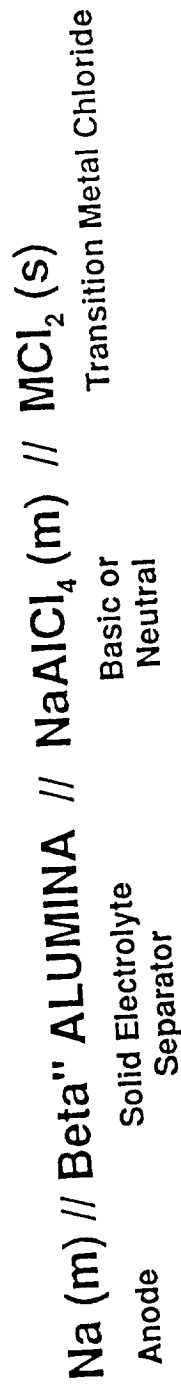


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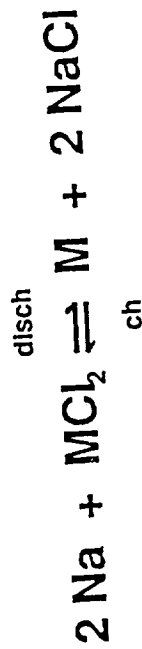
- CONFIGURATION AND ADVANTAGES
- CAPABILITIES OF THE SYSTEMS
- STUDIES AT JPL
- AREAS OF FURTHER STUDY

SODIUM - METAL CHLORIDE BATTERIES

- CONFIGURATION



- CELL REACTION



- METAL CHLORIDES

FERROUS CHLORIDE
NICKEL CHLORIDE

- OPERATING TEMPERATURES : $\geq 250^\circ\text{C}$

COMPARISON WITH Na - S

ADVANTAGES

- LOWER OPERATING TEMPERATURES
($\geq 250^{\circ}\text{C}$)
- WIDER RANGE OF OPERATING
TEMPERATURES (180 - 425 $^{\circ}\text{C}$)
- SAFETY IN THE EVENT OF INTERNAL SHORT
AND TEMPERATURE EXCURSIONS
- FAILS SHORT CIRCUIT (NO NEED FOR
BYPASS)
- BUILT-IN OVERCHARGE MECHANISM
- TOLERANCE TO OVERDISCHARGE
- ASSEMBLY IN THE DISCHARGED STATE WITH
LITTLE OR NO SODIUM

DISADVANTAGES

- MORPHOLOGICAL CHANGES
AT THE CATHODE
- LOWER POWER DENSITIES

CAPABILITIES OF THE SYSTEMS

SUMMARY OF DEVELOPMENT IN THE U.K. / SOUTH AFRICA

- FERROUS CHLORIDE

ENERGY DENSITIES OF 150 - 170 Wh/kg AT 2 - 4 h RATES WITH ELECTRODE POROSITIES ABOVE 80 % AND CONVERSION PERCENTAGES OF 30 - 40 %

1000 CYCLES AND ONE YEAR OF OPERATION IN A 5 Ah CELL

HIGH RATE DISCHARGE CAPABILITY IN AN 8 Ah CELL

FLAT DISCHARGE CURVES (1.8 V) AT THE 1 h RATE (180 mA/cm²)

- NICKEL CHLORIDE

2047 CYCLES IN A 7.5 Ah CELL WITH SULFUR ADDITIVE

75 % OF THE ORIGINAL CAPACITY RETAINED AT THE 1 h RATE

NO DEGRADATION OF BETA ALUMINA

NO LOSS IN THE SINTERED STRUCTURE OF THE ELECTRODE

CAPABILITIES OF THE SYSTEMS

PERFORMANCE OF MCl_2 CELLS AND BATTERIES

PARAMETER \rightarrow TYPE \downarrow		CAPACITY Amp. Hr	PRACTICAL ENERGY DENSITY @ 5 hr RATE		SPECIFIC POWER @2/3 OCV AND 70%DOD W / Kg
			Wh / Kg	Wh / l	
BETA 33 CELL 33 mm dia and 160-200 mm long	FeCl_2	42	142	260	139
	NiCl_2	40	124	310	150
BETA 55 CELL 55 dia and 230-300 mm long	FeCl_2	140	110	172	-
	NiCl_2	100	109	155	-
BETA 55 BATTERY	FeCl_2	15 KWh	88	103	-
	NiCl_2	30 KWh	88	95	-

A. R. Tilley and R. N. Bull, 22nd IECEC; 1078 (1987)

ENVIRONMENTAL TESTS ON Na/MCl₂ CELLS

- CRUSHING : NO CELL BREACHING; TEMP. RISE OF 75°C
- SHORT CIRCUIT :
 - INTERNAL : TEMPERATURE RISE TO 500°C
 - EXTERNAL : NO EFFECT
- OVERHEATING TO 750°C : NO CELL BREACHING; SLIGHT LEAKAGE
- FREEZE-THAW CYCLING : NO FAILURE AFTER 50 CYCLES
- OVERCHARGE : NO EFFECT (SLIGHT LEAKAGE ABOVE > 100%)
- OVERDISCHARGE : NO EFFECT
- SHOCK AND VIBRATION : NO FAILURE IN BOTH FIXED AMPLITUDE AND VEHICLE SIMULATION TESTS

R. J. WEDLAKE AND A. R. TILLEY, B. ELECTROCHEM., 4, 41 (1988)

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Na / NiCl₂ CELLS FOR SPACE APPLICATIONS AT ESTEC

- FEASIBILITY STUDIES : 100 - 120 Wh/Kg
- PROTOTYPE CELLS : 59 - 70 Wh/Kg

- AFTER 2810 GEO AND LEO CYCLES
 - NO DEGRADATION FOR BETA ALUMINA
 - RECHARGE RATIO ~ UNITY
 - ROUND TRIP ENERGY EFFICIENCY HIGH
 - CAPACITY DECLINED BY 40 %.

- NEED FOR CELL OPTIMIZATION

- ELECTRODE THICKNESS
- ALTERNATE ELECTROLYTE GEOMETRIES

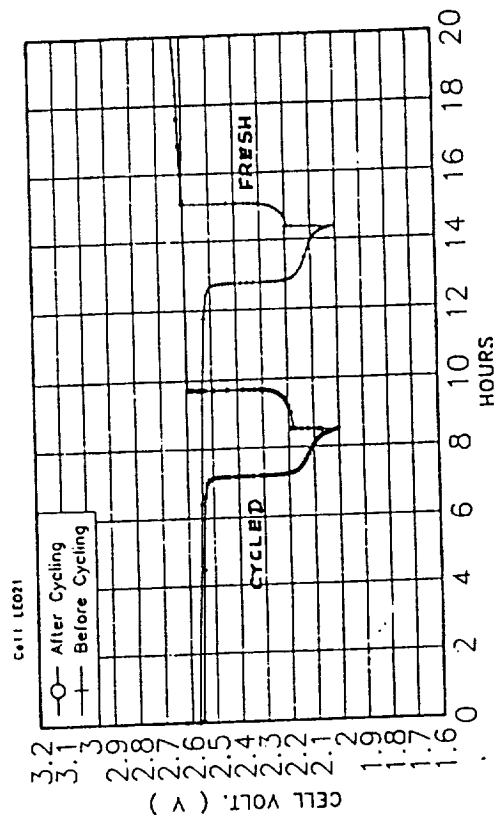


Fig. 8 CELL CAPACITY AT 1 A RATE BEFORE & AFTER
2810 CYCLES

B. Hendel and G. DUDLEY, NASA Workshop, December 1990



JPL EFFORT

OBJECTIVE

- TO DEVELOP A HIGH SPECIFIC ENERGY BATTERY FOR FUTURE NASA MISSIONS

APPROACH

- TO IDENTIFY, EVALUATE AND DEVELOP ALTERNATE CATHODE MATERIALS TO SULFUR FOR RECHARGEABLE SODIUM BATTERIES

INITIAL STUDIES

- ORGANIC CATHODE MATERIALS
EVALUATED TCNE AND TCNQ AS POSSIBLE ALTERNATIVES
PROBLEMS OF THERMAL INSTABILITY, POLYMERIZATION LIKELY
- INORGANIC CATHODE MATERIALS
TRANSITION METAL CHLORIDES IN CHLOROALUMINATE MELTS



JPL EFFORT - PRESENT APPROACH

METAL CHLORIDE CATHODES

- FUNDAMENTAL STUDIES IN SINGLE ELECTRODE CONFIGURATION TO ESTABLISH THE MECHANISMS FOR THE REDUCTION OF FeCl_2 AND NiCl_2

PREDICT THE FEASIBILITY OF USING OTHER TRANSITION METAL CHLORIDES

IDENTIFY RATE-LIMITING PROCESSES

DETERMINE THE ELECTRODE KINETICS

STUDY THE EFFECTS OF ADDITIVES

- PERFORMANCE EVALUATION IN LABORATORY TEST CELLS
- IDENTIFY THE FAILURE MODES

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MECHANISM OF FeCl_2 REDUCTION

- EVIDENCE FOR TWO - STEP REACTION MECHANISM FROM CYCLIC VOLTAMMETRY
 Na_6FeCl_8 INTERMEDIATE

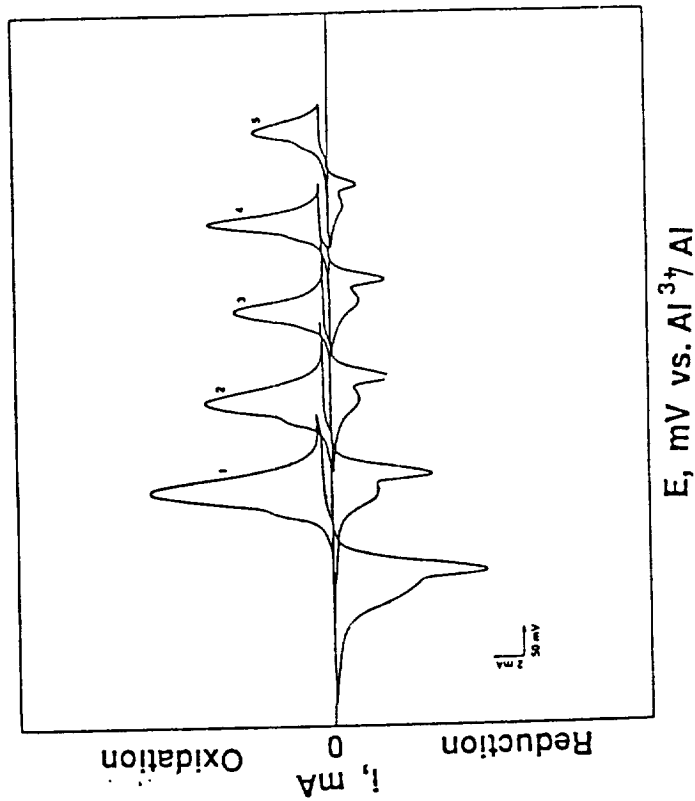
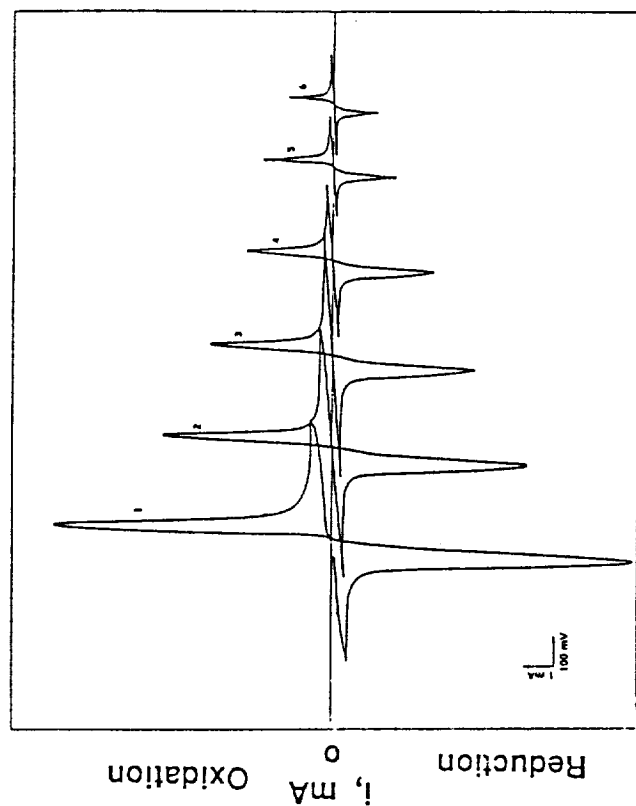


Fig. 3. Cyclic voltammograms of Fe electrode (area: 0.05 cm^2) in NaAlCl_4 at 220°C at scan rates of 1.) 20, 2.) 10, 3.) 5, 4.) 2, and 5.) 1 mV/s . Scale on the y axis is 1 mA/cm (reduced to half) for curves 4 and 5.

- Ni ADDITIONS FOR OVERCHARGE PROTECTION OF FeCl_2

MECHANISM OF NiCl_2 REDUCTION

- SINGLE - STEP REACTION SCHEME CONFIRMED BY CYCLIC VOLTAMMETRY



Cyclic voltammetric curves of Ni electrode in NaAlCl_4 at 220°C at different scan rates of 1) 50, 2) 20, 3) 10, 4) 5, 5) 2 and 6) 1 mV/s.

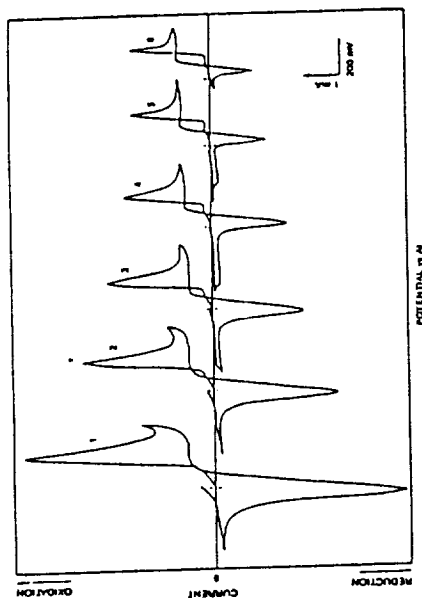
- GOOD REVERSIBILITY

OTHER METAL CHLORIDES

REQUIRED CRITERIA FROM CYCLIC VOLTAMMETRY

- .. Low oxidation currents subsequent to peak indicate low solubility for the chloride
- .. Reversible peaks and single step
- Ti, V, Mn, Cr, Al and Ag UNLIKELY.
- .. High oxidation currents.

Co

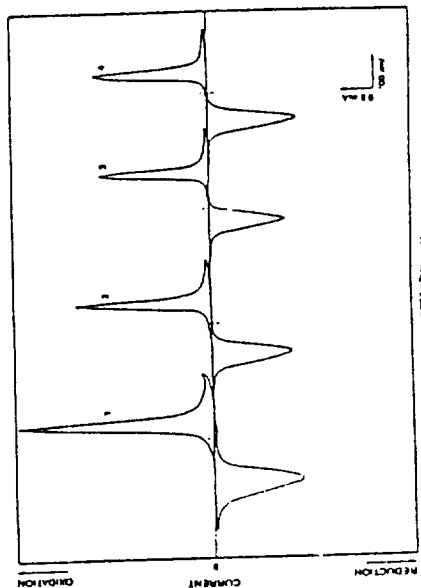


Voltammograms of Co (E_0 : 870 mV) at 1) 50, 2) 20, 3) 10, 4) 5, 5) 2 and 6) 1 mV/s.

- COPPER EXHIBITS TWO - STEP OXIDATION (SECOND STEP FORMS SOLUBLE CHLORIDE)

.. Unlikely.

Mo



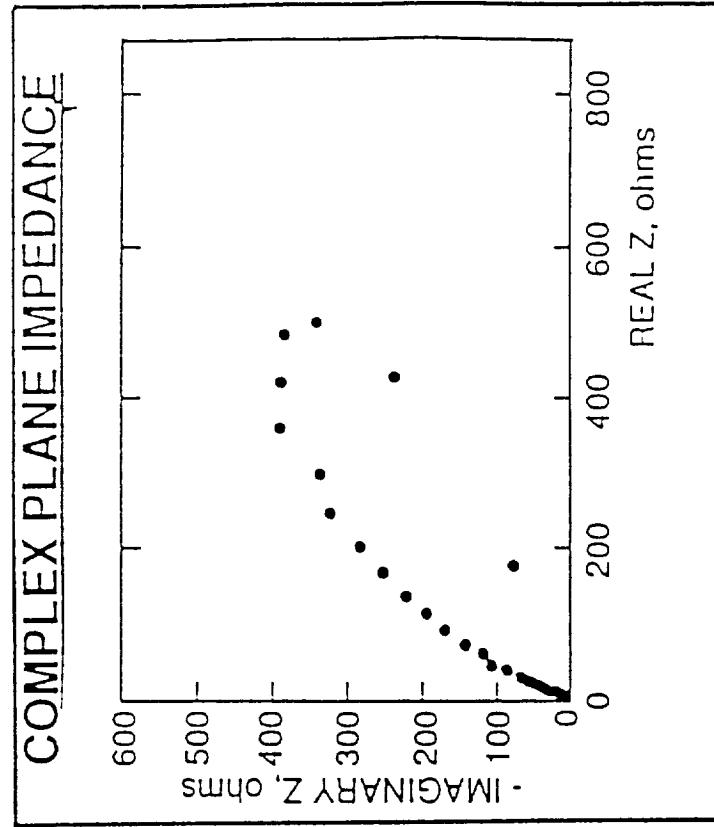
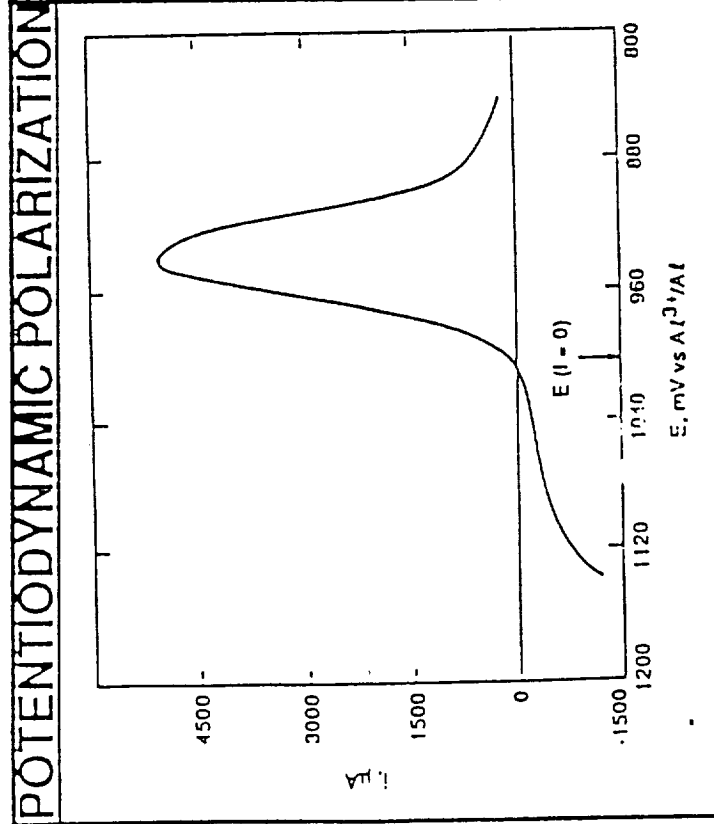
Voltammograms of Mo (E_0 : 997 mV) at 1) 50, 2) 20, 3) 10 and 4) 5 mV/s (Scale on Y-axis doubled for curve 4).

- COBALT AND MOLYBDENUM ARE LIKELY CATHODE MATERIALS

.. Low oxidation currents.

- MOLYBDENUM IS A STABLE CURRENT COLLECTOR FOR NiCl_2 .

PASSIVATION OF NiCl_2



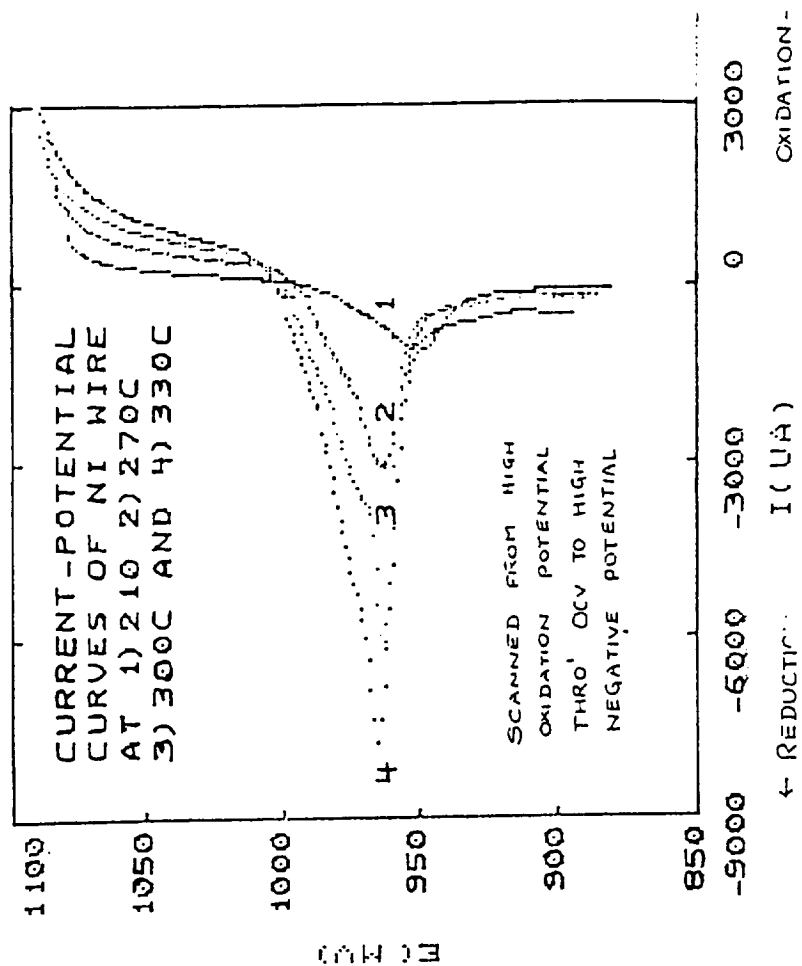
- PASSIVATION DURING REDUCTION BY NaCl PRECIPITATION
- PASSIVATION IS MORE PROMINENT THAN IN FeCl_2

PASSIVATION OF NiCl_2

- PASSIVATION INCREASES AT LOWER STATES OF CHARGE AND LOWER ELECTRODE POTENTIALS.

- PASSIVATION IS ALLEVIATED BY INCREASING THE PORE SIZE OF THE ELECTRODE

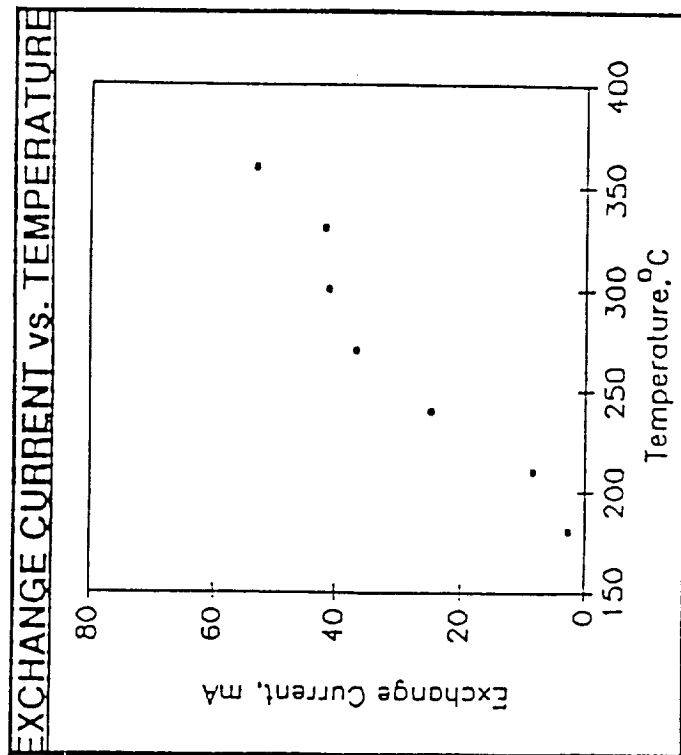
- PASSIVATION CAN BE REDUCED BY OPERATING AT HIGHER TEMPERATURES



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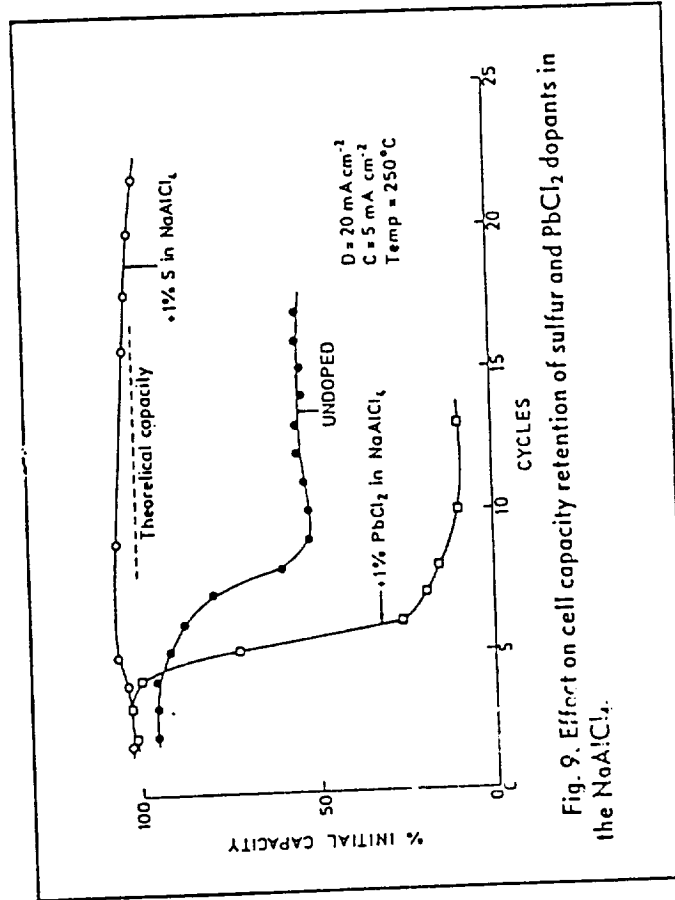
KINETICS OF MCl_2 REDUCTION

- HIGH EXCHANGE CURRENT DENSITIES (1 mA/cm^2) FOR BOTH FeCl_2 AND NiCl_2 .
- 10 % INCREASE IN THE EXCHANGE CURRENT DENSITY OF NiCl_2 FOR EACH 10°C RISE IN THE OPERATING TEMPERATURE.
- OPTIMUM TEMPERATURE FOR $\text{NiCl}_2 \geq 250^\circ\text{C}$.



ADDITIVE REQUIRED FOR NiCl_2

- DECLINE IN CAPACITY PREMATURELY
- EFFECT MORE PROMINENT AT HIGHER POROSITIES
- LOSS OF SINTERED STRUCTURE DUE TO AN AGGLOMERATION OF NI PARTICLES

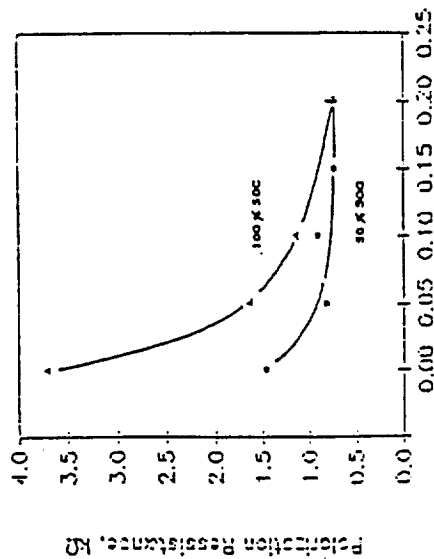


R. J. Bones, D. A. Teagle, S. D. Brooker and F. L. Cullen
J. Electrochem. Soc., 136, 1274 (1989).

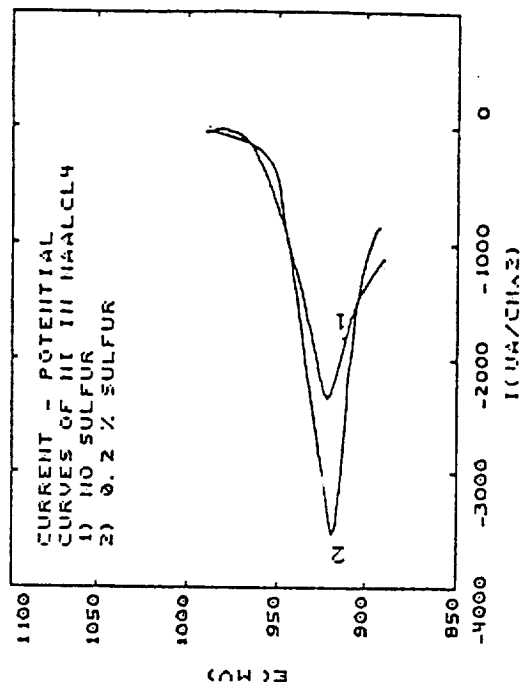
- SULFUR REDUCES MORPHOLOGICAL CHANGE

EFFECT OF SULFUR ON NiCl_2 KINETICS

- HIGHER PEAK CURRENTS IN CYCLIC VOLTAMMETRIC CURVES
- IMPROVEMENT IN RECHARGEABILITY
- ENHANCED KINETICS OF NiCl_2 REDUCTION
- REDUCED PASSIVATION
- MAXIMUM SULFUR CONTENT ~0.2 w% IN THE ELECTROLYTE



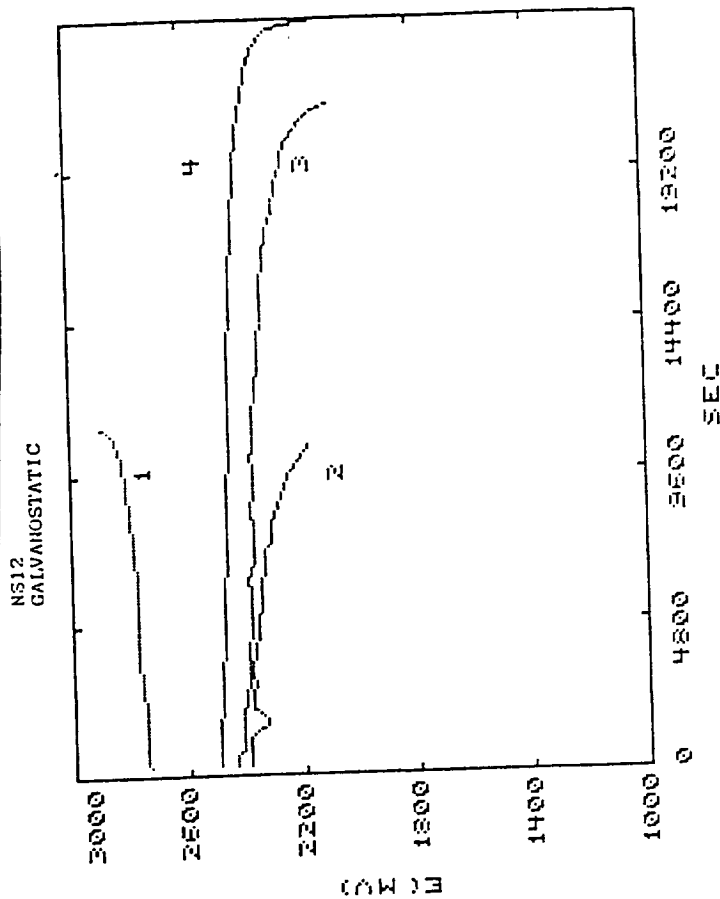
Amount of sulfur, wt%



CURRENT - POTENTIAL CURVES OF Ni IN H_2SO_4
1) 110 Sulfur
2) 0.2 % Sulfur

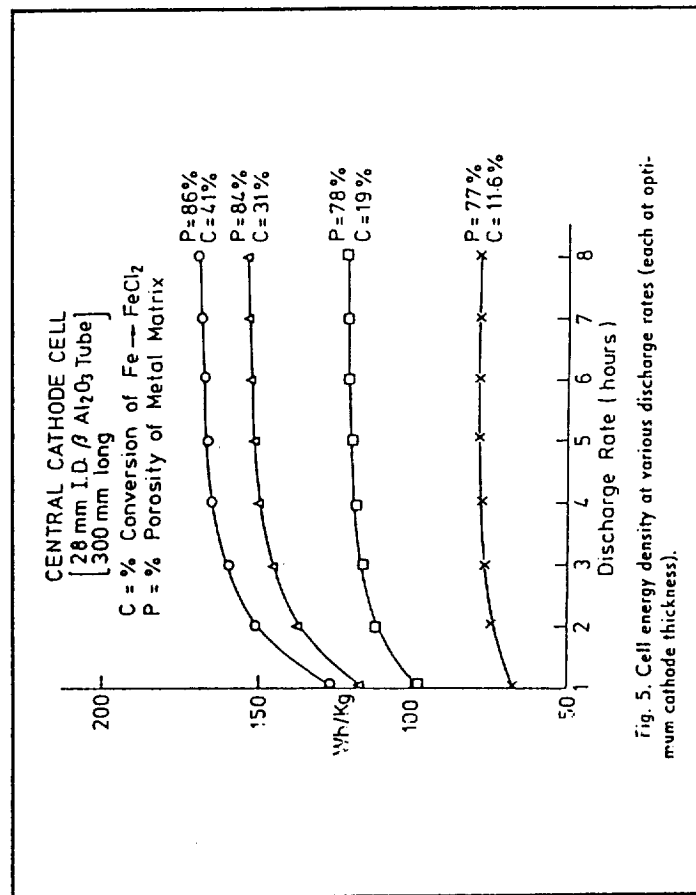
PRELIMINARY PERFORMANCE DATA OF 1 Ah CELL

- HIGH ROUND TRIP EFFICIENCY (~ 95%)
- 50 % CONVERSION OF NaCl
- HIGH DISCHARGE YIELDS OF ABOVE 80 % AT THE 4 - 5 h RATES
- FORMATION APPEARS TO BE INCOMPLETE AND REQUIRES OPTIMIZATION



FABRICATION PARAMETERS VS. ENERGY DENSITY

- OPTIMIZE CONVERSION EFFICIENCY (RATIO OF NaCl : M) AND ELECTRODE POROSITY

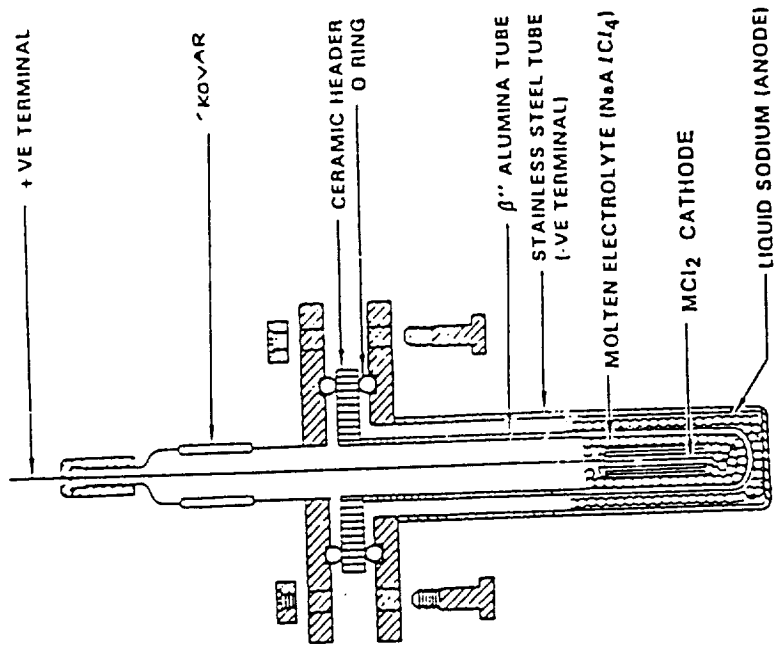


R. J. Bones, J. Coetzer, R. C. Galloway
and D. A. Teagle, J. Electrochem. Soc.,
134, 2379 (1987).

- STATE OF THE ART ELECTRODES:
33 % CONVERSION AND 90 % POROSITY

5 Ah CELL AS TEST VEHICLE

- CYLINDRICAL CENTRAL CATHODE;;
CATHODE - LIMITED DESIGN
(Na : ~ 200 - 300%)
- BETA ALUMINA TUBES WITH ALPHA
ALUMINA HEADER
- MECHANICAL COMPRESSION SEAL
- KOVAR TO GLASS SEAL FOR
CATHODE



AREAS OF STUDY

- IMPROVEMENT IN POWER DENSITIES
 - ALTERNATE ELECTRODE DESIGNS
 - OTHER METHODS OF ELECTRODE FABRICATION
 - ALTERNATE ELECTROLYTE GEOMETRIES
 - FLAT PLATE BETA WITH POSSIBLY Na ALLOYS
- IMPROVEMENT IN CYCLE LIFE
 - NON-SULFUR ADDITIVES FOR MORPHOLOGICAL BENEFITS
 - ELECTRODE FABRICATION
 - CELL DESIGN FOR SCREENING OF ADDITIVES
- DESIGN OPTIMIZATION FOR HIGH SPECIFIC ENERGIES
 - CELL / BATTERY DESIGN
 - SEALING METHODS
 - COMPONENTS RATIO
 - CELL CONFIGURATION
- RELIABILITY
 - FAILURE ANALYSIS

ACTIVITY	88	89	90	91	92	93	94	95	96	97	98	99	2000
SCREENING STUDIES	IDENTIFY SYSTEM CAPABLE OF PROVIDING > 1000 CYCLES AND 150 Wh/Kg												
ELECTROCHEMICAL CHARACTERIZATION OF MCl_2	ESTABLISH MECHANISMS DETERMINE REACTION KINETICS AND IDENTIFY RATE LIMITING PROCESSES												
COMPONENT DEVELOPMENT	DEFINE DESIGN REQUIREMENTS FOR 20-25 Ah CELLS												
PERFORMANCE AND SAFETY EVALUATION	DEMONSTRATE CYCLE LIFE AND PERFORMANCE IN OPTIMIZED 20-25 Ah CELL												
PROTO TYPE	FINAL DEMONSTRATION												

PUBLICATIONS FROM JPL ACTIVITIES

1. "AEROSPACE APPLICATIONS OF SODIUM BATTERIES USING NOVEL CATHODE MATERIALS",
PROC. OF 24th IECEC, WASHINGTON D.C., AUG. 1989.
2. "ORGANIC CATHODE MATERIALS IN SODIUM BATTERIES"
J. APPLIED ELECTROCHEMISTRY, 20 , 357 - 364 (1990).
3. "ADVANCED RECHARGEABLE SODIUM BATTERIES WITH NOVEL CATHODES"
J. POWER SOURCES, 29, 301 - 309 (1990).
4. "ELECTROCHEMISTRY OF METAL CHLORIDES IN SODIUM BATTERIES".
J. ELECTROCHEM. SOC., 137, 2991 - 2997 (1990).
5. "ALTERNATE CATHODES FOR SODIUM - METAL CHLORIDE BATTERIES"
J. ELECTROCHEM. SOC., 138, 883 - 884 (1991).
6. "SODIUM - METAL CHLORIDE BATTERY RESEARCH AT JPL"
PROC. SERT CONF., APRIL 1991.
7. "PROGRESS AND RECENT DEVELOPMENTS IN SODIUM - METAL CHLORIDE BATTERIES"
PROC. 26th IECEC, BOSTON, MA, AUG. 1991.

CONCLUSIONS

- RAPID DEVELOPMENT IN THE TECHNOLOGY OF Na / MCl_2 BATTERIES HAS BEEN ACHIEVED IN THE LAST DECADE MAINLY DUE TO THE :
 - .. EXPERTISE AVAILABLE WITH Na / S SYSTEM
 - .. SAFETY AND
 - .. FLEXIBILITY IN DESIGN AND FABRICATION
- LONG CYCLE LIVES OF OVER 1000 AND HIGH ENERGY DENSITIES OF ~ 100 Wh/Kg HAVE BEEN DEMONSTRATED IN BOTH Na / FeCl_2 AND Na / NiCl_2 CELLS.
- OPTIMIZATION OF POROUS CATHODE AND SOLID ELECTROLYTE GEOMETRIES ARE ESSENTIAL FOR FURTHER ENHANCING THE PERFORMANCE.
- FUNDAMENTAL STUDIES CONFIRM THE CAPABILITIES OF THESE SYSTEMS. NiCl_2 EMERGES AS THE CANDIDATE CATHODE MATERIAL FOR HIGH POWER DENSITY APPLICATIONS SUCH AS ELECTRIC VEHICLE AND SPACE.

